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(54) Title of the Invention: ANTI-FOGGING GLASS AND MANUFACTURING METHOD THEREOF

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SPECIFICATION

1. Title of the Invention
ANTI-FOGGING GLASS AND MANUFACTURING METHOD THEREOF

2. Claims

(1) An anti-fogging glass characterized by the fact that a thin film of an inorganic oxide such as silica, titania and the like is applied so as to form fine irregularity to the glass surface having a specific thickness.

(2) A manufacturing method of anti-fogging glass characterized by the fact that a thin film of an inorganic oxide such as silica, titania and the like is applied to the glass surface by sputtering, having a specific thickness, followed by chemically etching the surface of said film with a corrosive agent such as hydrogen fluoride under specific condition.

3. Detailed Explanation of the Invention
(Industrial Field of Application)

This invention relates to an anti-fogging glass to be used with vehicles and the like and the manufacturing method thereof.

(Prior Art)

Due to the fact that, during rainy weather or in winter, rain droplets attach to the windscreen glass and the rear-view mirror glass to be used with vehicles and the like, and that water droplets form on the windscreen glass and the rear-view mirror glass caused by the moisture release of the passengers, causing the fogging of the

windscreen glass and the rear-view mirror glass, the see-through clarity for the driver drops, which can then interfere with the driving. In order to prevent such fogging of the windscreen glass and the rear-view mirror glass, for instance, a hydrophilic surface active agent was sprayed or coated onto the surface of the windscreen glass and the rear-view mirror glass in the past.

(Problems that the Invention is to Solve)

Nevertheless, the anti-fogging products, as using the above-mentioned methods, lack in durability, and have the problem that the anti-fogging effect does not last long. Also, although there is another method of attaching a transparent plastic sheet that contains a hydrophilic group that is formed with cellulose ester, it is scratch-prone due to the fact that such sheet is soft, lacking in scratch resistance, and is difficult to apply to the windscreen glass and the rear-view mirror glass for vehicles.

This invention is intended to solve the problems in the above mentioned prior art, and its objective is to present an anti-fogging windscreen glass and rear-view mirror glass and the manufacturing thereof that are fog-resistant in the rainy weather and winter, and has sufficient practical durability.

(Means for Solving the Problems)

Thus, the anti-fogging windscreen glass and rear-view mirror glass in this invention are characterized by the fact that a thin film of an inorganic oxide such as silica, titania and the like is applied so as to form fine irregularity to the glass surface having a specific thickness.

The glass used in this invention can be used for normal windscreen glass and rear-view mirror glass. A thin film is formed onto the surface of this glass from an inorganic oxide, such as above-mentioned silica (SiO_2), titania (TiO_2), and others such as alumina (Al_2O_3), indium oxide (In_2O_3; Sn dope) by sputtering. The preferred thickness of the film varies on the types of the inorganic oxide, but 4000~6000Å is appropriate when using silica, for instance. The durability of the film is insufficient with the film thickness of less than 4000Å, and the effectiveness does not improve by exceeding 6000Å, on the other hand. With sputtering, it is preferable to conduct it at the glass plate temperature of 500°C and greater when the argon sputter gas pressure is about $7x10^{-3}$ Torr, and at the glass plate temperature of 150°C and greater when the gas pressure is about $15x10^{-3}$ Torr.

The film of an inorganic oxide that is formed on the glass surface consists of fine crystal particles. When followed by the chemical etching of the surface of said thin film using a corrosive agent such as hydrogen arsenate alone or in combination with a mixed-acid corrosive agent containing oxidized acids like nitric acid, sulfuric acid and the like, or with salts, the crystal boundary is corroded first due to the fact that it is more corrosion-prone than other sections, forming fine irregularity on the surface. In terms of the corrosion condition, when using a 0.15wt% hydrogen arsenate solution at normal temperature, it is preferable to immerse within this solution for approximately 30 minutes.

It becomes possible from the above operation to obtain an anti-fogging glass with the see-through clarity and sufficient durability.

(Embodiments)

We shall explain this invention in detail using embodiments hereafter. Incidentally, this invention is not limited to the embodiments below.

Embodiment 1: Relationship between the glass plate temperature and argon gas pressure

A windscreen glass plate was inserted into a vacuum container and is decompressed to 10^{-3} Torr. Then argon was introduced as the sputter gas so that the pressure reached $2x10^{-3}$, $7x10^{-3}$, $15x10^{-3}$ Torr in each, and a film was formed of SiO_2 by sputtering on the glass surface at an average thickness of approx. 5000Å. In this case, the glass plate temperature was varied at 60°C,

150°C, 300°C each. The glass plate was removed from the vacuum container after the film formation, which then was immersed for 30 minutes in a 0.15wt% hydrogen arsenate solution at normal temperature, corroding the film surface. Next, after the corroded surface was rinsed with distilled water, the glass plate was immersed in warm water at 60°C for a specific length of time, followed by the removal and further rinsing with distilled water. It was then dried.

In regards to each of the above samples, the angle of contact was measured between the distilled water and the SiO_2 film of the process glass, as shown in Figure 1. In the Figure, 1 denotes the glass plate, 2 denotes SiO_2 sputter film, 3 denotes water droplets, and 4 denotes the angle of contact. Also, the results are shown in Table 1.

Table 1

Argon Gas Pressure (Torr)	Glass Plate Temperature (°C)		
	60	150	300
$2x10^{-3}$	39	28	25
$7x10^{-3}$	35	22	12
$15x10^{-3}$	30	16	8

From Table 1, it is clear that the higher the temperature of the glass plate is during the SiO_2 sputter film formation, and also that the higher the argon gas pressure is during the film formation, the lower the angle of contact is versus the water droplets after corrosion, and the easier it gets wet. With those with the angle of contact of 16° or less, the droplets are effectively flat, causing no problem to the visibility.

Incidentally, the unprocessed glass plate showed the angle of contact of 42°, and with the glass plates with the SiO_2 film formed but before being corroded, the angle is 40°. With these glass plates, the water droplets on the surface apparently function as lenses, compromising the visibility. In addition, when the glass is used for the windscreen glass for vehicles, while the normal glass fogs up when it comes to fogging of the interior side due to the body perspiration and the like, the processed glass plate of this invention with the angle of contact of 16° or less merely becomes wet, lacking the formation of small water droplets and the fogging up thereby.

We shall explain the anti-fogging phenomenon in this invention as follows.

The SiO_2 sputter film 2 has a virtually vertical column structure on the surface of the glass plate 1 that is normally the base plate, as shown in Figure 2. When the SiO_2 sputter film 2 of the above-mentioned structure is corroded under a specific condition within a corrosive agent such as the HF solution, the corrosion of the crystal boundary, that is, in between the columns of the column-like crystal particles, advances ahead of others, as shown in Figure 3. The surface before corrosion 5 transforms to the surface after corrosion 6, forming irregularity to the corroded surface. It is believed that the wettability is the result of the formation of this fine irregularity. Thus, this phenomenon is the same as the ground glass, which has good wettability and whose surface does not attract water droplets.

Also, we can explain the difference in the angles of contact due to the sputtering condition as follows.

When the temperature of the glass plate rises, the structure of the sputter film 2 is such that the thickness of the column-like crystals, that is, the size of the crystal particles, increases, and the irregularity caused by the corrosion becomes rough, as shown in Figure 2. When the argon gas pressure increases, the same phenomenon also occurs.

Where the temperature of the glass plate is low, or where the argon gas pressure is low, extremely small column-like crystals form. Following the corrosion, extremely fine irregularity is formed on the surface of the SiO_2 sputter film 2, and it is believed that the effectiveness against wetness ceases to appear because of this.

What is judged to have the see-through clarity effect is one with an angle of contact of 16° or less. In order to obtain such condition, it is ideal to have, as the conditions for the SiO_2 sputter film formation, the glass plate temperature of

150°C and higher when the argon gas pressure is 15×10^{-3} Torr, and the glass plate temperature of 300°C and higher when the argon gas pressure is 7×10^{-3} Torr.

Embodiment 2: Relationship among concentration of hydrogen arsenate, length of immersion, angle of contact, and fogging value

SiO_2 was formed into a film of a 5000Å thickness by sputtering onto a glass plate at the argon gas pressure of 15×10^{-3} Torr and the glass plate temperature of 500°C. A corrosion test followed by varying the concentration of the hydrogen arsenate solution and length of immersion, measuring the fogging value using a haze meter as standardized by ASTM-D1003-61 as well as measuring the angle of contact with water droplets. There were four measuring points for the fogging value. Incidentally, the fogging value for a normal windscreen glass is approx. 0.15~0.1%. The results are shown in Table 2.

Table 2: Angles of contact (top row: degrees) and fogging value (bottom row: %) under various corrosion conditions

immersion time (minutes) / Concentration (wt%)	3	10	30	60
2	15~3 0.2~7	5~3 5~7	3 7~8	3 7~8
0.3	19 0.3	8 1.5~ 2.5	5~7 ~2	5~1 3~4
0.15	35 0.15~ 1	17 0.15~ 0.1	8 0.15~ 0.1	8 0.15~ 0.1
0.01	40 0.15~ 1	40 0.15~ 1	32 0.15~ 0.1	21 0.15~ 0.1

From Table 2, it is clear that the corrosion of the sputter film is rapid when using a 2 wt% hydrogen arsenate solution, and that slight fogging was visible to the naked eye after approximately 10 minutes. Also, there is a dispersion in the fogging values. Moreover, the entire surface fogged up after an immersion of 30 minutes or longer, taking an appearance of a ground glass. On the contrary, where a 0.3 wt% hydrogen arsenate solution was used, even though the fogging value did not become too high, the stability was lacking in the angle of contact in that water droplets formed in some local spots when the water was sprayed, leading us to believe that the consistency was missing on the processed surface. With the 0.15 wt% concentration of the hydrogen arsenate solution, the angle of contact was 8° in the immersion time of longer than 30 minutes up to 60 minutes, with the fogging value stabilizing at 0.15~0.1%. Also, the finish appeared extremely consistent, and the wet condition of the surface when the water droplets were sprayed was also consistent. In addition, when the concentration of the hydrogen arsenate solution was lowered to 0.01 wt%, it is believed that the corrosion was generally not progressing with the immersion time of less than 30 minutes. Also, the specific effect was not obtainable even with the immersion of 60 minutes, being inferior in terms of productivity.

Thus, as to the corrosion conditions, it is preferable in the light of the property and productivity to immerse for 30 minutes with a 0.15 wt% hydrogen arsenate solution at normal temperature.

Also, as to the corrosive agent, it goes without saying that one may use a mixed-acid corrosive agent containing oxidized acids like nitric acid, sulfuric acid and the like, or salts, other than hydrogen arsenate.

Embodiment 3: Manufacture of anti-fogging windscreen glass using various inorganic oxides

Using TiO_2 , Al_2O_3, In_2O_3 (Sn dope) instead of SiO_2, conducting the same experiment as in Embodiments 1 and 2, it became possible to obtain an anti-fogging windscreen glass

with the improved wettability generally equivalent to SiO_2.

Embodiment 4: Relationship between thickness of SiO_2 sputter film and fogging value

With the film thickness of SiO_2 being varied in the same method as in Embodiment 1, and an anti-fogging windscreen glass was manufactured, and a taper abrasion test was conducted according to JISR3212. Figure 4 shows the relationship between the film thickness before and after the corrosion and the fogging value. As it is obvious from the Figure, the fogging value was under +2% of the standard before the corrosion, but the one with the film thickness below 4000Å showed the fogging value of 3~5%, showing poor scratch resistance. Also, even when the film thickness was great, the effect did not change. Therefore, the preferred film thickness of SiO_2 is 4000 Å~6000Å.

(Effects of the Invention)

As seen above, because the anti-fogging glass of this invention is one whose surface is coated with a thin film that consists of an aggregate of crystal particles of an inorganic oxide having a specific thickness while at the same time having fine irregularity on the surface, it is superior in wettability, and has become ideal for the vehicle windscreen glass and rear-view mirror glass. Thus, even when water was sprayed to the surface of the anti-fogging glass of this invention, no droplets formed, leading to a significant improvement in the see-through clarity versus unprocessed glass.

In addition, in contrast to the products of the past that had the glass surface coated with an anti-fogging agent or a hydrophilic plastic sheet attached, the product of this invention is superior in durability because of the fact that it has a hardened inorganic oxide thin film on the glass surface. For instance, the anti-fogging effect is maintained even after 3,000 hours of the windscreen wiper use.

Also, due to the fact that a thin film of an inorganic oxide is formed on the glass surface by sputtering, the manufacturing method of the anti-fogging glass of this invention is simple and quick. Also, it is possible to variously combine different types of inorganic oxides, and to easily vary the property of the thin film by choosing a condition. In addition, because the irregularity is formed by chemically etching the surface of the thin film, various acids, salts, and combinations thereof can be used as a corrosive agent, allowing for the choice of corrosion condition and for the easy obtainment of an anti-fogging glass with a desired property.

Because this invention is intended to present an anti-fogging glass that resists fogging in rainy weather and in winter, with sufficient practical durability, it not only improves the driving visibility and safety when applied as a vehicle product, but also it adds to the product value of the vehicle. Also, it can be widely used in other fields where good visibility is needed, producing various effects as a special glass material.

4. Brief Explanation of the Drawings

Figure 1 is a cross-section of a drawing showing the angle of contact between the SiO_2 sputter film and water droplets on its surface.

Figure 2 is a drawing showing the structure of the SiO_2 sputter film formed on the surface of a glass plate.

Figure 3 is a drawing showing the shape transformation of the surface of the SiO_2 sputter film before and after chemical etching.

Figure 4 is a diagram showing the relationship between the film thickness of the SiO_2 sputter film and fogging value.

In the Figures:

1 – Glass plate 2 – SiO_2 sputter film
3 – Water droplets 4 – Angle of contact
5 – Surface before corrosion
6 – Surface after corrosion

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Figure 1

2 SiO_2 sputter film
1 Glass plate

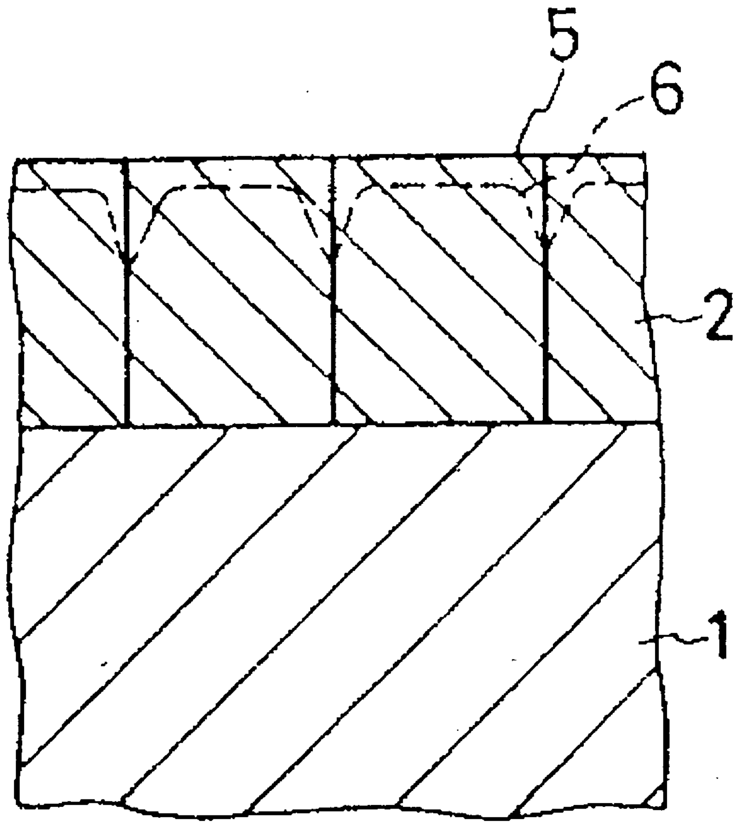
Figure 2

Figure 3

Figure 4

(vertical axis) Fogging value
(horizontal axis) SiO_2 film thickness

O...before corrosion
_...after corrosion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